



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : A44B 18/00	A1	(11) International Publication Number: WO 00/57742 (43) International Publication Date: 5 October 2000 (05.10.00)
(21) International Application Number: PCT/US00/07268 (22) International Filing Date: 17 March 2000 (17.03.00) (30) Priority Data: 99200931.6 26 March 1999 (26.03.99) EP (71) Applicant: MINNESOTA MINING AND MANUFACTURING COMPANY [US/US]; 3M Center, P.O. Box 33427, Saint Paul, MN 55133-3427 (US). (71)(72) Applicants and Inventors: VON JAKUSCH, Egbert, A. [DE/DE]; Obenflachsberg 98, D-42653 Solingen (DE). JUNG, Dieter [DE/DE]; Moerser Strasse 31c, D-47447 Moers (DE). (74) Agents: BOND, William, J. et al.; Office Of Intellectual Property Counsel, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).		(81) Designated States: AE, AL, AM, AT, AT (Utility model), AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, CZ (Utility model), DE, DE (Utility model), DK, DK (Utility model), DM, DZ, EE, EE (Utility model), ES, FI, FI (Utility model), GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KR (Utility model), KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (Utility model), SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: LOOP FASTENING MATERIAL (57) Abstract <p>The present invention provides a loop fastening material usable as the loop portion of a hook and loop fastener, the loop fastening material comprising in order: (1) a loop layer comprising (a) a multiplicity of flexible loops of fibers having a denier of less than 15 and adapted to be releasably engaged by the complementary hook portion of the hook and loop fastener, and (b) a backing layer in which the flexible loops are anchored; and (2) a pressure sensitive adhesive layer characterised in that the loop layer comprises a silicone release composition including a reaction product of a curable composition of (i) a polydialkylsiloxane having acrylate and/or methacrylate groups and (ii) an organic compound free of silicon and comprising at least two reactive groups selected from the group consisting of an acrylate and a methacrylate group.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

LOOP FASTENING MATERIAL

1. Field of the Invention

5 The present invention relates to loop fastening material usable as the loop portion of a hook and loop fastener containing a loop layer at its first major side and a pressure sensitive adhesive layer at its second major side. In particular, the present invention relates to a loop fastening material in which the loop layer contains a particular silicone release composition. The invention further relates to a method of making the loop
10 fastening material and to an assembly of loop fastening material. The loop fastening material is especially suitable for use in the production of absorbent articles such as diapers and accordingly the present invention also relates to an absorbent article including the loop fastening material.

2. Background of the Invention

15 Many sheets of loop materials are known that are adapted to be cut into pieces to form the loop portions for fasteners of the type comprising releasably engageable hook and loop portions. Such sheets of loop materials typically comprise a backing and a multiplicity of loops formed from longitudinally oriented polymeric fibers anchored in the
20 backing and projecting from a front surface of the backing so that they may be releasably engaged with the hooks on the hook portion of such a fastener, and can be made by many methods including conventional weaving, or knitting techniques. Sheets of loop materials in which the loops are stitched into the backing are described in U.S. Pat. Nos. 4,609,581 and 4,770,917.

25 U.S. Patent No. 5,256,231 describes loop fastening materials that can be produced at lower cost than the aforementioned loop materials and that also have good aesthetic qualities. The loop fastening material of this US-patent are produced by corrugating either a non-woven web or series of substantially parallel yarns in a corrugating nip and
30 subsequently extrusion bonding a thermoplastic film onto specific anchor portions of the sheet of corrugated fibrous material. A particularly inexpensive and highly effective loop structure can be produced by using fibers of less than 25 denier, preferably from 1 to 10 denier in size with the loop material having a basis weight of from 5 to 300 grams per square meter. This type of loop material is particularly suitable for use as the loop portion
35 in a hook and loop closure system where the number of closures and reclosures are limited such as in the case of an absorbent article, e.g. a diaper.

When intended for use in the production of a disposable absorbent article, e.g. a diaper, the loop fastening material generally comprises in order (1) a loop layer forming its first major surface and the loop layer comprising (a) a multiplicity of flexible fibrous loops adapted to be releasably engaged by the complementary hook portion of the hook and loop fastener, and (b) a backing layer in which the flexible fibrous loops are anchored; and (2) a pressure sensitive adhesive layer forming a second major surface of the loop fastening material. The loop fastening material is typically offered as an assembly of a plurality of sheets of loop fastening material arranged on top of each other or as a roll where a sheet of loop fastening material is wound upon itself. To avoid contamination of the loop layer with the adhesive layer in such assemblies, a release liner may be provided between the loop layer and the adhesive layer. However this has the disadvantage of creating additional waste and making such assemblies more expensive.

EP 693889 discloses an assembly of loop fastening material comprising one or more multilayer sheets of loop fastening material suitable for use as the loop portion of a hook and loop fastener, wherein the loop fastening material comprises, in order: (1) a loop layer on the first major surface of the material that comprises (a) a multiplicity of flexible loops adapted to be releasably engaged by the complementary hook portion of the hook and loop fastener and (b) a base layer to which loops are anchored, and (2) a pressure sensitive adhesive layer on the second major surface of the material. In the assemblies of this European patent application, the adhesive layer of an overlying portion of the loop fastening material is in direct contact with the loop layer of an underlying portion of the loop fastening material and the loops are such that when the overlying portion of the loop fastening material is removed from the assembly, the loops of the underlying portion are presented in an engageable state. To achieve that the loops present them in an engageable state, EP 693889 teaches that it may be necessary to control the adhesion between the loops and the pressure sensitive adhesive layer. This may be done according to the European application by coating the loop layer with a release agent. Exemplified release agents include reactive silicones, epoxy silicones and radiation curable polyorganosiloxane-polyurea block copolymers as disclosed in EP 250248.

Although this type of assembly offers the advantage of being more cost effective and creating less waste, it was found that in particular with loop fastening materials having a loop layer of flexible loops of low denier, e.g. 12 or less, it would be desirable to improve the loop integrity and to reduce fiber contamination of the adhesive layer of the overlying loop fastening material.

U.S. Patent No. 4,696,854 discloses a porous bilayer non-woven substrate of an organic polymer layer and a cured silicone resin layer. An adhesive tape that can be wound upon itself can be produced by coating a hydrophilic natural or synthetic pressure

sensitive adhesive on the organic polymer layer. US 4.871.611 similarly relates to non-woven adhesive tapes intended for medical applications. This US-patent discloses coating of the non-woven substrate on one side with a radiation curable polysiloxane resin composition and curing the composition while avoiding substantial penetration into the non-woven backing. The exemplified coating compositions contain practically 100% of polysiloxane resin. The preferred silicone resin of US 4.871.611 includes (meth)acrylated polydialkylsiloxanes such as the TEGO™ Silicone Acrylates RC-149, RC-300, RC-450 and RC 802 available from Goldschmidt AG.

WO 88/7931 relates to release coatings that comprises 1 to 30 % by weight of a reactive silicone dispersed as a discontinuous phase in 99 to 70% by weight of a reactive resin. Exemplified reactive silicones include polydimethylsiloxanes having an acrylic group, a mercapto group or an oxirane group. The reactive resin comprises reactive oligomers that have functional groups capable of reacting with the reactive silicone. The release coating can be provided on paper or polymeric film to produce, for example, labels.

WO 95/23694 relates to a silicone release coating that comprises a mixture of two different classes of (meth)acrylated silicones. Exemplified reactive silicones include the silicones available from Goldschmidt Chemical Corp. under the tradename TEGO™ RC. Particularly disclosed is TEGO™ RC-726 as an example of one class of silicones to be combined with RC-705, an example of the second class of silicones. The silicone release coating of this application may further optionally contain a reactive oligomer such as for example an acrylated or methacrylated polyhydroxy compound.

WO 96/5962 discloses radiation curable silicone release coatings that comprises a mixture of two different classes of (meth)acrylated silicones and a mono(meth)acrylate of a specific formula. Exemplified silicones include RC-726 and RC 708 both available from Goldschmidt Chemical Corp. and SL 5030 available from GE silicones. Reactive oligomers such a acrylated or methacrylated polyhydroxy compounds can also be added to the release composition. It is further taught that the release coating can be used on various substrates including paper, vinyl, PVC films, polyester films, polyolefin films, glass, steel, aluminum and non-woven fabrics.

US 5.562.992 discloses a radiation curable silicone release composition that comprises from 2 to 7% of a (meth)acrylated silicone resin and from 90 to 98% of an acrylated or methacrylated organic polyhydroxy compound or polyamino compound. Exemplified silicones include RC 450, RC 450N, RC 706, RC 707, RC 710, RC 720 and RC 726 all available from Goldschmidt Chemical Corp.. The release coating is said to be useful on various substrates including paper, vinyl, PVC films, polyester films, polyolefin films, glass, steel, aluminum and non-woven fabrics.

3. Summary of the Invention

The present invention provides a loop fastening material usable as the loop portion of a hook and loop fastener, said loop fastening material comprising in order: (1) a loop layer comprising (a) a multiplicity of flexible loops of fibers having a denier of less than 15, preferably not more than 12 and adapted to be releasably engaged by the complementary hook portion of the hook and loop fastener, and (b) a backing layer in which said flexible loops are anchored; and (2) a pressure sensitive adhesive layer characterised in that said loop layer comprises a silicone release composition including a reaction product of a curable composition of (i) a polydialkylsiloxane having acrylate and/or methacrylate groups and (ii) an organic compound free of silicon and comprising at least two reactive groups selected from the group consisting of an acrylate and a methacrylate group.

The present invention further provides a loop fastening material assembly comprising one or more multilayer sheets of a loop fastening material as described above and wherein said loop fastening material is arranged in said assembly such that the adhesive layer of an overlying loop fastening material is in direct contact with the loop layer of an underlying loop fastening material.

Further, the invention provides a method of making a loop fastening material provided with a silicone release composition comprising the steps of: providing a loop fastening material usable as the loop portion of a hook and loop fastener and having a loop layer comprising (a) a multiplicity of flexible loops of fibers having a denier of less than 15, preferably not more than 12 and adapted to be releasably engaged by the complementary hook portion of the hook and loop fastener, and (b) a backing layer in which said flexible loops are anchored; providing a pressure sensitive adhesive layer on said backing layer; coating a curable silicone release coating composition on said loop layer and; curing the thus applied silicone release coating by exposing it to actinic radiation or heat, said silicone release coating composition comprising (i) a polydialkylsiloxane having acrylate and/or methacrylate groups and (ii) an organic compound free of silicon and comprising at least two reactive groups selected from the group consisting of an acrylate and a methacrylate group.

The invention also provides an absorbent article having a loop fastening material, as described above, adhered to its outside surface.

4. Detailed description of the Invention

The loop fastening material of this invention typically comprises in order: (1) a loop layer forming a first major surface of the loop fastening material, the loop layer

comprising (a) a multiplicity of flexible loops of fibers having a denier of less than 15 and adapted to be releasably engaged by the complementary hook portion of the hook and loop fastener, and (b) a backing layer in which the flexible loops are anchored; and (2) a pressure sensitive adhesive layer forming a second major surface of the loop fastening material.

To reduce the aforementioned problems of fiber contamination of the adhesive layer of an overlying loop fastening material in an assembly and to improve integrity of the loops, the loop layer of the loop fastening material includes a specific silicone release composition. The silicone release composition of the loop layer comprises the cured reaction product of a polydialkylsiloxane having acrylate and/or methacrylate groups and an organic compound free of silicon comprising at least two reactive groups selected from the group consisting of an acrylate and a methacrylate. Preferred polydialkylsiloxanes include those that have a ratio of the average number of siloxane units to the average number of acrylate or methacrylate groups between 10 and 15. Particularly preferred for use in this invention are polydimethylsiloxanes having a ratio of the average number of siloxane units to the average number of acrylate or methacrylate groups between 10 and 15. Suitable polydialkylsiloxanes for use in this invention typically have a viscosity in the range of 100 to 500mPa s. Examples of suitable silicones for use in this invention are commercially available and include TEGO™ RC-902 and RC-715 both available from Goldschmidt Chemical Corp.

The organic compound free of silicon for reaction with the polydialkylsiloxane is typically an acrylated or methacrylated polyhydroxy compound or an acrylated or methacrylated polyamino compound. The organic compound has at least two and more preferably at least three acrylate and/or methacrylate groups. The organic compound should preferably also have a viscosity of at least 500mPa s at 25°C and more preferably at least 800mPa s at 25°C, and most preferably at least 1500mPa s at 25°C. Particular examples of organic compounds for use in the invention include ditrimethylol propane tetraacrylate available as E 140 from UCB Chemicals, Belgium, E-80 an amine-modified polyester acrylate, available from UCB Chemicals and E 810, a polyester tetraacrylate available from UCB. Modified pentaerythritol triacrylate (viscosity ca. 500 mPas) available as SR-444 from Sartomer, aliphatic diacrylate oligomer (viscosity ca. 1000 mPas) available as CN-132 from Sartomer, ethoxylated bisphenol A dimethacrylate (viscosity ca. 1100 mPas) available as SR-348 from Sartomer, bisphenol A derivative diacrylate oligomer (viscosity ca. 1400 mPas) available as E-150 from UCB.

The weight ratio of polydialkylsiloxane to organic compound in the curable composition from which the cured product is prepared is conveniently between 8:92 and 70:30, preferably between 10:90 and 60:40 and more preferably between 10:90 and 45:55.

Forming the second major surface of the loop fastening material there is provided a pressure sensitive adhesive layer. Suitable pressure sensitive adhesives for use in the adhesive layer of the adhesive tape are the pressure sensitive adhesives commonly used in adhesive tapes for diapers. The pressure sensitive adhesive should be capable of providing a loop fastening material tape having a 90° peel adhesion of at least 3 N/2.54cm as tested according to the procedure set forth in the example section. This 90° peel adhesion is the adhesion obtained after the adhesive layer has been in contact with the silicone release composition of the loop layer, i.e. the adhesive tape should retain a 90° peel adhesion of at least 3 N/2.54cm after being unwound from a roll or after being removed from a stack of loop fastening materials. Preferably, the pressure sensitive adhesive layer of this invention comprises a rubber resin based adhesive of which the tackiness has been modified by the inclusion of a tackifying resin. The rubber resin preferably comprises an A-B-A block copolymer wherein the A blocks are derived from a styrene monomer and the B blocks are derived from isoprene, butadiene or hydrogenated version of these.

Such adhesives are disclosed generally in U.S. Pat. Nos. 3,419,585, 3,676,202, 3,723,170 and 3,787,531.

Particularly preferred adhesive compositions for use in this invention are disclosed in US 5,019,071 and US 5,300,057. The preferred adhesive composition comprises a thermoplastic elastomeric component and a resin component and the thermoplastic elastomeric component consists essentially of about 50-90 parts, preferably about 60-80 parts, of a linear or radial styrene-isoprene-styrene A-B-A block copolymer and about 10-50 parts, preferably about 20-40 parts of a simple styrene-isoprene A-B block copolymer. The A-blocks are derived from styrene or styrene homologues and the B-blocks are derived from isoprene, either alone or in conjunction with small proportions of other monomers, in both the A-B-A and A-B block copolymers.

As indicated above, the A-B-A block copolymers preferably are of the type which consists of A-blocks (end blocks) derived, i.e., polymerized, from styrene or styrene homologues; and B-blocks (center blocks) derived from isoprene either alone or in conjunction with small proportions of other monomers. The individual A-blocks preferably have a number average molecular weight of at least about 7,000, preferably in the range of about 12,000-30,000, and the A-blocks preferably constitute about 10-35 percent by weight of the block copolymer. The number average molecular weight of the B-blocks for linear A-B-A block copolymers preferably is in the range of about 45,000-180,000 and that of the linear copolymer, itself, preferably is in the range of about 75,000-200,000. The number average molecular weight of the radial A-B-A block copolymers preferably is in the range of about 125,000-400,000, and that of the corresponding B-blocks preferably is about 95,000-360,000.

Useful radial A-B-A polymers are for example of the type described in U.S. Pat. No. 3,281,383 and conform to the following general formula: (A-B)-(n) X, wherein A is a thermoplastic block polymerized from styrene or styrene homologues, B is an elastomeric block polymerized from a conjugated diene such as butadiene or isoprene, X is an organic or inorganic connecting molecule, with a functionality of 2-4 as described in U.S. Pat. No. 3,281,383 or possibly with a higher functionality as described in the article entitled "New Rubber is Backed by Stars" appearing on page 35 of the June 11, 1975 issue of Chemical Week. "n" then is a number corresponding to the functionality of X.

In the styrene-isoprene derived A-B block copolymers, the number average molecular weight of the individual A-blocks is typically about 7,000-20,000 and the total molecular weight of the block copolymer generally should not exceed about 150,000. A-B block copolymers based on styrene and isoprene are described generally in U.S. Pat. No. 3,787,531.

The elastomeric component of the preferred adhesive composition may include small amounts of other more conventional elastomers but these should not exceed about 25 percent by weight of the elastomeric component. These include natural rubbers, synthetic rubbers based on butadiene, isoprene, butadiene-styrene, butadiene-acrylonitrile and the like, butyl rubbers, and other elastomers.

The preferred adhesive composition includes about 20-300 parts preferably 50-150 parts, of resin component, per one hundred parts by weight of the thermoplastic elastomeric component. The resin component consists essentially of tackifier resins for the elastomeric component. In general any compatible conventional tackifier resin or mixture of such resins may be employed. These include hydrocarbon resins, rosin and rosin derivatives, polyterpenes, and other tackifiers.

The adhesive layer may also include small amounts of various other materials such as anti-oxidants, heat stabilizers and ultraviolet absorbers, fillers, and the like. Typical antioxidants are 2,5 ditertiary amyl hydroquinone and ditertiary butyl cresol. Similarly, conventional heat stabilizers such as the zinc salts of alkyl dithiocarbamates may be used. Similarly, the particulate mixture of this invention may include small amounts of fillers and pigments such as zinc oxide, aluminum hydrate, clay, calcium carbonate, titanium dioxide, carbon black and others.

The adhesive layer is typically provided at a thickness of 20 to 200 μ m and more preferably at a thickness of 25 μ m to 100 μ m.

The loop layer of the loop fastening material of this invention comprises a loop layer of releasably engagable, upstanding loops which may be formed by any of several methods known in the art such as weaving, knitting, warp knitting, weft insertion knitting, stitching, or methods for making non-woven structures. Typically, the loop fastening

material comprises a backing layer with a multiplicity of loops extending therefrom. Illustrative examples of loop fastening materials for use with this invention include knits such as warp knits, weft inserted knits, tricot knits and circular knits, stitched materials and non-woven materials.

5 The loop layer of this invention is preferably extrusion bonded to a thermoplastic film layer forming the backing layer. Such a loop fastening material can be produced by providing a loop fastening material in accordance with the method disclosed in US 5,256,231, coating the loop layer with the curable silicone release composition and curing the silicone release coating by means of heat or by exposure to actinic radiation.

10 The method for providing the loop fastening material as taught in US 5,256,231 comprises the steps of: providing a nonwoven sheet of fibers; forming a sheet of fibers to have arcuate portions projecting in the same direction from a surface defined by spaced anchor portions of the sheet of fibers; extruding a thin layer of molten thermoplastic material onto the spaced anchor portions of the fibers to form at least a portion of a
15 backing around the spaced anchor portions of the sheet of fibers with the arcuate portions of the sheet of fibers projecting from a front surface of the backing; cooling and solidifying the layer of thermoplastic material to form the sheet of loop material.

 The step of forming the sheet of fibers to have arcuate portions comprises: providing first and second generally cylindrical corrugating members each having an axis
20 and including a plurality of spaced ridges defining the periphery of the corrugating member, the ridges having outer surfaces and defining spaces between said ridges adapted to receive portions of the ridges of the other corrugating member in meshing relationship with the sheet of fibers therebetween; mounting the corrugating members in axially parallel relationship with portions of the ridges in meshing relationship; rotating at least
25 one of the corrugating members; feeding the sheet of fibers between the meshed portions of the ridges to generally conform the sheet of fibers to the periphery of the first corrugating member and form the arcuate portions of the fibers in the spaces between the ridges of the first corrugating member and the anchor portions of the sheet of fibers along the outer surfaces of the ridges of the first corrugating member; and retaining the formed
30 sheet of fibers along the periphery of the first corrugating member for a predetermined distance after movement past the meshing portions of the ridges.

 The loop fastening material provided in accordance with the method set forth above, includes a backing comprising a thermoplastic backing layer with generally uniform morphology, and a sheet of longitudinally oriented fibers having generally non-
35 deformed anchor portions bonded or fused in the thermoplastic backing layer at spaced bonding locations, and arcuate portions projecting from a front surface of the backing between the bonding locations.

When the sheet of loop material is used to form loop portions of fasteners intended for limited use (i.e., for uses in which the fastener will ordinarily be opened and closed 10 times or less), preferably the arcuate portions of the sheet of fibers have a height from the backing of less than about 0.64 centimeters (0.250 inch) and preferably less than about 5 0.38 centimeters (0.15 inch); the width of the bonding locations should preferably be between about 0.005 and 0.075 inch; and the width of the arcuate portions of the sheet of fibers should be between about 0.06 and 0.35 inch. Also, the fibers in the arcuate portions should preferably project to about the same height above the front surface of the backing, which height is at least one third, and preferably one half to one and one half the distance 10 between the bonding locations, the individual fibers should be less than 15 denier in size, preferably not more than 12 denier, and the fibers collectively preferably have a basis weight in the range of 5 to 300 grams per square meter (and preferably in the range of 15 to 100 grams per square meter) measured along the front surface of the backing to provide sufficient open area between the fibers along the arcuate portions (i.e., between about 10 15 to 70 percent open area) to afford ready engagement of the fibers along the arcuate portions by the hook portion of the fastener.

The fibers for forming the loop layer of the loop fastening material may be of many polymeric materials including polypropylene, polyethylene, polyester, nylon or polyamide or a combination of such materials such as a core of polyester and sheath of 20 polypropylene. Fibers of one material or fibers of different materials or material combinations may be used in the same sheet of fibers from which the loop layer is formed.

The backing layer which is extrusion bonded to the loop layer may be of the type that solidifies as it cools or can be of the type called reactive hot melts that partially solidify as they cool and then cross link as a result of exposure to an external element such 25 as atmospheric moisture or actinic radiation. The backing layer may for example be formed from polypropylene or polyethylene. The backing layer may further be bonded to further backing layers so as to provide a multilayer backing.

To produce the loop fastening material of this invention, the loop layer of the fastening material is coated with the curable silicone release composition. The silicone 30 release coating composition can be applied by any conventional means known in the coating art. Particular examples of suitable coating techniques include, roller coating, brushing, spraying, reverse roll coating, gravure coating and die coating. In a particularly preferred embodiment of this invention, the silicone release coating composition is substantially free of solvents and is applied by multi roll coating. By the term 35 substantially free of solvents is meant that the coating composition contains less than 10% by weight and more preferably less than 5% by weight of solvents.

The silicone release coating composition is typically applied in an amount to give a dried coating of between 1 g/m² and 3 g/m². Preferably, the amount applied is such that the measured (according to the procedure set forth in the examples) amount of cured silicone release coating is between 0.3 g/m² and 2 g/m², preferably between 0.5g/m² and 1.5g/m².

Curing of the coated silicone release composition can be effected by heat or photochemically by irradiation with actinic radiation such as for example electronic beam, UV light, x-ray, gamma-ray and beta ray. In a preferred embodiment of the present invention, the silicone release coating composition also comprises a thermal or photochemical free radical initiator. Examples of useful photochemical free radical initiators, i.e. photoinitiators, which may be used in combination with ultraviolet light include, for example, benzyl ketals, benzoin ethers, acetophenone derivatives, ketoxime ethers, benzophenone, benzo or thioxanthenes, etc. Specific examples of photoinitiators include: 2,2-diethoxyacetophenone; 2- or 3- or 4-bromoacetophenone; benzoin; benzophenone; 4-chlorobenzophenone; 4-phenylbenzophenone; benzoquinone; 1-chloroanthroquinone; p-diacetyl-benzene; 9,10-dibromoanthracene; 1,3-dephenyl-2-propanone; 1,4-naphthyl-phenylketone; 2,3-pentenedione; propiophenone; chlorothioxanthone; xanthone; fluorenone; and mixtures thereof. An example of a commercially available photoinitiator of this type is available from the Ciba Geigy Corporation of Hawthorne, N.Y. under the trade name of Darocur 1173. An alternative photoinitiator is a mixture of 70% oligo 2-hydroxy-2-methyl-1-4-(1-methylvinyl) phenyl propanone and 30% 2-hydroxy-2-methyl-1-phenyl-1-propanone available as ESACURE KIP 100F from Lamberti spa (Albizzate, Italy).

When present, the free radical initiator is typically used in an amount of 1 to 10 parts by weight for 100 parts by weight of the silicone release composition and more preferably in an amount of 2 to 5 parts by weight for 100 parts by weight of the silicone release composition.

The radiation-curable silicone release coating compositions of the present invention can be stabilized against premature polymerization during storage by the addition of conventional polymerization inhibitors such as hydroquinone, monomethylether of hydroquinone, phenothiazine, di-t-butyl paracresol, etc. Amounts of 0.1 weight percent or less of the stabilizers are generally effective.

The pressure sensitive adhesive layer is then provided on the side of the loop fastening material opposite to the side with the loop layer. The pressure sensitive adhesive layer can be applied by means of any of the coating techniques known in the art or the adhesive layer can be first coated to a release liner and then transfer laminated. Suitable coating techniques include hot melt coating techniques as well as solvent or water borne

coating techniques such as knife coating, die coating, spraying, curtain coating and flat bed coating.

5 The loop fastening material of this invention is conveniently supplied as an assembly in which one or more sheets of the loop fastening material are arranged with the adhesive layer of an overlying loop fastening material being in direct contact with the loop layer of an underlying loop fastening material. Such an assembly includes for example a stack of sheets of the loop fastening material stacked on top of each other. However, one or more sheets of the loop fastening material can also be wound upon themselves to form an assembly in the form of a roll.

10 The loop fastening material of the invention can be used in any instance where it is desired to attach a loop component of a hook and loop mechanical fastener system to a substrate. In particular, the loop fastening material can be attached to the outside surface of a (disposable) absorbent article such as a disposable diaper. The loop fastening material can be applied to a diaper in a variety of ways and have one or more of several function in a single diaper.

15 Frequently, loop fastening material is applied to the portion of a diaper designated to be the central waistband area on the front side of a disposable diaper. This use is commonly referred to as a frontal tape, as illustrated for example, in Figure 1 of U. S. Patent 5,053,028 (Zoia et al.).

20 The loop fastening material of this invention can also be employed as a component of the diaper closure system which is attached to the ear portions of the diaper and can be incorporated into laminates. For example, the loop fastening material can be employed as part of a three tape mechanical closure laminate such as disclosed in UK Patent Application GB 2 257 895 and European Patent Application 98 121 337.4 filed by 3M on November 10, 1998, where, upon first use, the frontal tape separates from the laminate and adheres permanently to the frontal area of the diaper.

25 The loop fastening material can further be incorporated into a closure laminate to prevent opening or flagging of the folded laminate after it is adhered to the diaper ear such as described in European Patent Application No. EP 795,307. The loop fastening material can also be incorporated into a closure laminate to provide disposability of the soiled diaper such as disclosed in European Patent Application 529 681 and European Patent Application EP 321 324.

30 The invention is further illustrated by means of the following examples without the intention to limit the invention thereto.

Examples

Test Methods

Measurement of Amount of Release Composition on the Surface of a Loop Layer

5 The amount of release composition present on the surface of the loop layer was measured using an X-ray fluorescence analyser Model 200TL available from ASOMA Instruments, Austin, Texas. The test method is available from Th. Goldschmidt AG, Essen, Germany, in two parts: a calibration technique available as KM RC 005 A and a measurement technique available as SM 316 A.

10 The calibration technique involves first coating and curing known quantities of UV curable polydimethylsiloxane (PDMS)(available as TEGO-RC 726 from Th. Goldschmidt) on a polyester film. At least five differing known coating weights were coated, UV-cured and measured for their x-ray fluorescence. A calibration curve relating x-ray fluorescence to amount of PDMS present was then prepared.

15 The measurement technique employs x-ray fluorescence of silicon atoms. A test substrate having some unknown amount of silicone on its surface is subjected to x-ray fluorescence. The absolute value of the fluorescence is measured and the corresponding amount of PDMS is read from the calibration curve.

20 The actual amount of release composition on the surface was then calculated from the amount of measured PDMS using the following formula:

$$\begin{aligned} &\text{Release Composition on Surface in g/m}^2 \\ &= \\ &(\text{g PDMS/m}^2 \text{ measured on coated substrate} - \text{g PDMS/m}^2 \text{ measure on uncoated} \\ &\text{substrate}) / \text{Factor for the release composition} \end{aligned}$$

25

The elements to be fed into the formula are determined by the following:

- 30 1. g PDMS/m² measured on coated substrate is read from the calibration curve relating amount of fluorescence to amount of PDMS present
2. g PDMS/m² on uncoated substrate is that value measured for the loop fastening material with no release composition (corresponding to a "blank" measurement)
- 35 3. A factor is given by Th. Goldschmidt in the test method (an "RC number") for each of the UV-curable (meth)acrylated silicones. This is essentially the fraction of the UV-curable silicone which is PDMS. The factor is always less than 1.0 and is lower for UV-curable silicones which have less silicone content (more acrylate groups). The factor for the release composition is calculated in a weighted average fashion using the amount

and factor for each of the materials employed. Additives which have no polydimethyl siloxane units (free of silicon atoms) are given a factor of zero.

90° Release (modified Keil test)

5 This test represents a method for measuring the force required to separate an adhesive tape from a release-coated surface.

A first sample of loop fastening material 5 cm wide and 10 cm long was adhered to a steel substrate by placing the adhesive surface on the plate and rolling over twice with a 2 kg roller.

10 A second sample loop fastening material 5 cm wide and 10 cm long was then placed on top of the first sample in a manner such that the adhesive layer of the second sample contacted the release coating of the first sample. The laminate of samples was rolled down two times with a 2 kg roller.

15 The laminate was then placed in a forced air oven at 50°C and a 1400 g weight was then allowed to rest on top of the laminate for 3 days while it was heated to 50°C.

The test laminate was then removed from the oven and allowed to rest at 23°C and 50% relative humidity for 24 hours before testing.

20 The adhesive of the second sample was peeled from the loop layer of the first sample using the 90° peel adhesion method described under 90° Peel Adhesion Test above at a peel speed of 300 mm/min.

Each material was evaluated three times and the results averaged. Data was recorded in N/50 mm.

90° Peel Adhesion

25 Peel adhesion was measured using a portion of loop fastening material unwound from a roll of loop fastening material as prepared in the examples. The loop fastening material sample was first subjected to the modified Keil test described above. After the uppermost loop fastening material was removed from the lower tape strip at a 90° angle in the Keil test, the uppermost loop fastening material was immediately adhered to the polyethylene test surface as described below. The test evaluated the ability of the loop fastening material to adhere to a polyethylene film after the adhesive had been in contact with the silicone-based release material under heat and pressure.

30 The polyethylene film used in this test was prepared as follows. A low density polyethylene resin (Tenite 1550P available from Eastman Chemical Co. Kingsport, Tennessee) having a melt index of 3.5 grams/10 min and a density of 0.918 grams/cm³ was extruded at a melt temperature of 182°C vertically downward through a conventional coat-hanger slot extrusion die. The melt exiting the die was drawn into a nip formed by a

mirror finish chrome roll(8°C inlet water temperature) and a silicone rubber roll(7°C inlet water temperature) resulting in a film of 330 microns thickness. The surface of the film contacting the chrome roll was used for test purposes. The surface of the film used for testing the peel adhesion had an average surface roughness value R_a of 1.4 μ m and an average peak to valley height value R_z of 12.5 μ m. The roughness values R_a and R_z were determined by a laser profilometer available from UBM Messtechnik GmbH, Ettlingen, Germany, model number UB-16. The roughness values were calculated by this machine in accordance with Deutsche Industrie Norm (DIN) 4768 and DIN 4762.

The substrate for the test was prepared by first firmly bonding the polyethylene film to the stainless steel test plate surface. The polyethylene film was adhered to the test plate with double-coated adhesive tape (available as Tape 410 from 3M Company).

90° Peel adhesion was measured using a tensile tester adapted in a special configuration to allow a peel angle of 90° to be maintained during the test. The equipment configuration is described in FINAT TEST METHOD NO. 2, a standard 90° peel test method (available from Federation Internationale des Fabricants Europeens et Transformateurs d'Adhesifs et Thermocollants sur Papiers et autres Supports (FINAT)).

There were several exceptions to the described FINAT method which are given below:

- 1) FINAT 2 requires a glass substrate which has been replaced by polyethylene film
- 2) a "standard FINAT test roller" was replaced by a 2 kg roller
- 3) the sample was rolled down once in each direction at 300 mm/min rather than twice at 200 mm/min as called for by the FINAT method
- 4) the dwell time was essentially zero rather than 20 min and 24 hrs, respectively, as required by the FINAT method.

A sample of loop fastening material 30 cm long and 2.54 cm wide was adhered to the polyethylene surface (the surface of the film that contacted the chrome roll during production) of the test plate by rolling it down two times with a 2 kg roller. A portion of the loop fastening material end was left free for grasping in the test apparatus as described in the test method. After a dwell time of less than one minute, the loop fastening material was peeled from the polyethylene substrate at a speed of 300 mm/min.

90° peel was recorded in units of N/2.54 cm. Three samples were evaluated and the results averaged.

Materials utilized in the Examples

(Meth)acrylate-functional Silicones

RC-715 is an acrylate-functionalized polydimethylsiloxane having a functionality of 26:2 (13.0) available as TEGO RC-715 from Th. Goldschmidt AG, Essen Germany

5 RC-902 is an acrylate-functionalized polydimethylsiloxane having a functionality of 56:4 (14.0) available as TEGO RC-902 from Th. Goldschmidt AG, Essen Germany

“Functionality” is defined as the ratio of number of dimethyl siloxane units / number of (meth)acrylate groups.

10 Organic Compounds

E 140 Ditrimehtylol propane tetraacrylate (DMPTA), $M_w = 438$,
viscosity = 1100 mPa s, available as E 140 from UCB Chemicals,
Drogenbos, Belgium.

15 E80 Amine-modified polyester acrylate, viscosity = 3000 mPa s,
available from UCB Chemicals, Drogenbos, Germany.

UV Polymerization Initiator

20 DAROCUR 1173 2-Hydroxy-2-methyl-1-phenyl-propan-1-one UV Photo-initiator
available from from Ciba-Geigy, Basel, Switzerland.

Example 1

25 A loop material comprising a loop layer extrusion bonded to a backing and available as XML 6157 from 3M Company, St. Paul, MN / USA was employed to make a loop fastening material. The loop portion of the backing had a thickness of 380 microns. The polypropylene film portion of the backing had a weight of 40 g/m². The fibers of the loop layer comprised polypropylene staple fibers having a diameter of ca. 37 microns or ca. 9 Denier.

30 A mixture of 30 wt % UV-curable silicone (available as TEGO™ RC-902 from Th. Goldschmidt AG, Essen Germany), 70 wt % ditrimethylolpropanetetraacrylate (DMPTA, $M_w = 438$, viscosity = 1100 mPa s, available as E140 from UCB Chemicals) and 3 wt. % UV polymerization initiator (available as DAROCUR™ 1173 from Ciba-Geigy, Basel,
35 Switzerland) was prepared by mixing the three components using a motor driven propeller mixer for 10 min at a temperature of 23 °C to form a homogeneous, milky white suspension. The suspension was then applied to the loop layer of the backing in an

amount of 2.5 g/m² using a multi-roll coater. The coating weight was measured by difference in weight of the backing before and after coating with release composition.

5 The coating was then cured in inert atmosphere (nitrogen) using UV light by passing the coated loop fastening material under medium pressure 120 W/cm mercury lamps (available as MODEL F-450 from Fusion UV Systems, Inc., Gaithersberg, Maryland). The distance from lamp to the surface of the loop layer was 2.5 cm.

10 A single layer of pressure-sensitive adhesive was then applied to the side of the loop fastening material opposite to the side bearing the loop layer. The adhesive was based on a mixture of synthetic block copolymer and tackifying resin and was applied by conventional hot-melt coating techniques using a drop die in an amount of 33 g/m².

15 The loop fastening material thus prepared was wound into a roll and then slit into thinner rolls of 50 mm in width. The components used to make the loop fastening material are summarized in Table 1.

Portions of the roll thus prepared were unwound and subjected to a modified Keil test. Samples from the Keil test were then used to measure adhesion to a standard polyethylene surface as described in the Test Methods above.

20 Loop fastening material test results are summarized in Table 2.

Examples 2

25 Example 1 was repeated with the exception that another type of organic compound was employed. In Example 2, 70 parts of E80, an amine-modified polyester acrylate, viscosity of ca. 3000 mPa s (available as E80 from UCB Chemicals, Drogenbos, Germany) was used as the organic compound, in conjunction with 30 parts of RC-902 as in Example 1.

30 Loop fastening material was prepared by first coating and curing the release composition on the loop side as in Example 1 and then coating the pressure-sensitive adhesive on the opposite side as in Example 1.

Example 3

35 Example 1 was repeated, with the exception that the UV-curable silicone employed in the release composition was RC-715, rather than RC-902 of Example 1.

Comparative Example 1

Example 1 was repeated with the exception that the silicone release coating employed on the loop layer was a polyorganosiloxane-polyurea block polymer as disclosed in European Application No. 250,248 (Leir et al.). The coating was applied by gravure coating and dried to yield a dry coating weight of 0.5g/m².

A loop fastening material was prepared as in Example 1 by providing a pressure-sensitive adhesive on the side opposite to the side containing the loop layer. The loop fastening material was then wound into a roll and tested.

Test results are shown in Table 2. The measured force for release of the pressure-sensitive adhesive from the release coating was 23.1 N/50 mm, an unacceptably high value for release which makes rolls difficult to unwind and could result in physical damage to the loop surface.

Table 1

Ex.	PSA (g/m ²)	Silicone compound			Organic compound		Release Comp.	
		Type (wt %)	Funct.	Visc. (mP.s)	Type (wt %)	Visc. (mP.s)	Visc. (mP.s)	Meas. amount (g/m ²)
1	33	RC 902 (30)	14	350	E 140 (70)	1100	1077	1.5
2	33	RC 902 (30)	14	350	E 80 (70)	3000	2650	1.5
3	33	RC 715 (30)	13	150	E 140 (70)	1100	870	1.5

Table 2

Ex.	90° release (Keil test), N/50 mm	90° Peel from PE, N/25 mm
1	6.4	3.41

2	7.4	4.31
3	4.7	4.92
C1	23.1	4.71

WE CLAIM:

1. Loop fastening material usable as the loop portion of a hook and loop fastener, said loop fastening material comprising in order: (1) a loop layer comprising
5 (a) a multiplicity of flexible loops of fibers having a denier of less than 15 and adapted to be releasably engaged by the complementary hook portion of the hook and loop fastener, and
(b) a backing layer in which said flexible loops are anchored; and (2) a pressure sensitive adhesive layer characterised in that said loop layer comprises a
10 silicone release composition including a reaction product of a curable composition of (i) a polydialkylsiloxane having acrylate and/or methacrylate groups and (ii) an organic compound free of silicon and comprising at least two reactive groups selected from the group consisting of an acrylate and a methacrylate group.
- 15 2. A loop fastening material according to claim 1 wherein said curable composition is a composition capable of curing upon exposure to actinic radiation.
3. A loop fastening material according to claim 1 wherein the ratio of the average number of siloxane units to the average number of acrylate and methacrylate
20 groups of said polydialkylsiloxane is between 10 and 15.
4. A loop fastening material according to claim 1 wherein said organic compound has a viscosity of at least 500mPa s at 25°C.
- 25 5. A loop fastening material according to claim 1 wherein the weight ratio of said polydialkylsiloxane to said organic compound in said curable composition is between 8:92 and 70:30.
6. A loop fastening material according to claim 1 wherein said loop layer is
30 extrusion bonded to a thermoplastic film layer forming said backing layer.
7. A loop fastening material assembly comprising one or more multilayer sheets of a loop fastening material as defined in any of claims 1 to 6 and wherein said loop fastening material is arranged in said assembly such that the adhesive layer of an overlying
35 loop fastening material is in direct contact with the loop layer of an underlying loop fastening material.

8. A loop fastening material assembly according to claim 7 wherein said assembly is a roll comprising one or more of said sheets of loop fastening material wound upon itself.

5 9. A method of making a loop fastening material provided with a silicone release composition comprising the steps of:

providing a loop fastening material usable as the loop portion of a hook and loop fastener and having a loop layer comprising (a) a multiplicity of flexible loops of fibers having a denier of less than 15 and adapted to be releasably engaged by
10 the complementary hook portion of the hook and loop fastener, and (b) a backing layer in which said flexible loops are anchored;

providing a pressure sensitive adhesive layer on said backing layer;

coating a curable silicone release coating composition on said loop layer

and;

15 curing the thus applied silicone release coating by exposing it to actinic radiation or heat, said silicone release coating composition comprising (i) a polydialkylsiloxane having acrylate and/or methacrylate groups and (ii) an organic compound free of silicon and comprising at least two reactive groups selected from the group consisting of an acrylate and a methacrylate group.

20 10. An absorbent article having a loop fastening material as defined in any of claims 1 to 6 adhered to its outside surface.

25 11. A loop fastening material as defined in any of claims 1 to 6 adhered to a substrate.

INTERNATIONAL SEARCH REPORT

Int. National Application No

PCT/US 00/07268

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 A44B18/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 A44B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 693 889 A (MINNESOTA MINING AND MANUFACTURING COMPANY) 31 January 1996 (1996-01-31) cited in the application page 4, line 5 - line 26; claims 1,11 ---	1,7-9,11
A	EP 0 250 248 A (MINNESOTA MINING AND MANUFACTURING COMPANY) 23 December 1987 (1987-12-23) cited in the application page 6, line 7 - line 12; claims 1,16 ---	1
A	US 5 562 992 A (AVERY DENNISON CORPORATION) 8 October 1996 (1996-10-08) cited in the application column 6, line 31 -column 8, line 57; claims 1,7,8,11,12 --- -/-	1,2

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

13 July 2000

Date of mailing of the international search report

21/07/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Garnier, F

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 00/07268

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>US 5 256 231 A (MINNESOTA MINING AND MANUFACTURING COMPANY) 26 October 1993 (1993-10-26) cited in the application examples 1-3</p> <p style="text-align: center;">---</p>	<p>1,6,10, 11</p>
A	<p>DATABASE WPI Section Ch, Week 199614 Derwent Publications Ltd., London, GB; Class D22, AN 1996-136736 XP002122943 & JP 08 027657 A (DAIWABO CO LTD), 30 January 1996 (1996-01-30) abstract</p> <p style="text-align: center;">-----</p>	<p>1,10,11</p>

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 00/07268

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 693889	A	31-01-1996	US 5389416 A	14-02-1995
			AU 673585 B	14-11-1996
			AU 6250994 A	08-11-1994
			BR 9405961 A	30-01-1996
			DE 69403644 D	10-07-1997
			DE 69403644 T	15-01-1998
			JP 3029047 B	04-04-2000
			JP 8508907 T	24-09-1996
			CA 2158741 A	27-10-1994
			DE 9421906 U	16-01-1997
			DE 9421907 U	16-01-1997
			EP 0754415 A	22-01-1997
			ES 2103581 T	16-09-1997
			IL 108834 A	18-03-1997
			WO 9423609 A	27-10-1994
			US 5605729 A	25-02-1997
EP 250248	A	23-12-1987	AU 591989 B	21-12-1989
			AU 7447487 A	24-12-1987
			BR 8703101 A	08-03-1988
			CA 1339226 A	05-08-1997
			DE 3752135 D	11-12-1997
			DE 3752135 T	16-04-1998
			EP 0737700 A	16-10-1996
			ES 2110391 T	16-02-1998
			JP 2901236 B	07-06-1999
			JP 10310628 A	24-11-1998
			JP 10279915 A	20-10-1998
			JP 2799381 B	17-09-1998
			JP 8231726 A	10-09-1996
			JP 3024678 B	21-03-2000
			JP 10060386 A	03-03-1998
			JP 2784761 B	06-08-1998
			JP 63003029 A	08-01-1988
			KR 9609692 B	23-07-1996
			KR 9609691 B	23-07-1996
			TR 24305 A	01-08-1991
			US 5512650 A	30-04-1996
			US 5461134 A	24-10-1995
			US 5214119 A	25-05-1993
			US 5290615 A	01-03-1994
			ZA 8704414 A	22-02-1989
US 5562992	A	08-10-1996	US 5543231 A	06-08-1996
US 5256231	A	26-10-1993	AU 661969 B	17-08-1995
			AU 8306491 A	18-02-1992
			BR 9106659 A	30-03-1993
			CA 2085604 A	19-01-1992
			DE 69124608 D	20-03-1997
			EP 0539504 A	05-05-1993
			ES 2097214 T	01-04-1997
			GR 3023225 T	30-07-1997
			IL 98775 A	14-05-1996
			JP 6500025 T	06-01-1994
			KR 195810 B	15-06-1999
			MX 9100247 A	28-02-1992
			WO 9201401 A	06-02-1992

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 00/07268

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5256231 A		US 5354591 A	11-10-1994
		US 5643397 A	01-07-1997
		US 5611791 A	18-03-1997
		US 5254194 A	19-10-1993
		US 5616394 A	01-04-1997
		AU 622171 B	02-04-1992
		AU 3378389 A	16-11-1989
		BR 8902225 A	02-01-1990
		CA 1333952 A	17-01-1995
		DE 68908468 D	23-09-1993
		DE 68908468 T	03-03-1994
		EP 0341993 A	15-11-1989
		ES 2043010 T	16-12-1993
		IL 90159 A	08-07-1993
		JP 2018036 A	22-01-1990
		JP 2896159 B	31-05-1999
		KR 9613457 B	05-10-1996
		MX 173200 B	08-02-1994
		ZA 8903577 A	30-01-1991
JP 8027657 A	30-01-1996	JP 2971332 B	02-11-1999